

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>C23C 16/00, 16/44, C30B 25/02, 29/22, H01L 39/24, 39/12</b>		A1	(11) International Publication Number: <b>WO 00/15865</b>
			(43) International Publication Date: 23 March 2000 (23.03.00)
(21) International Application Number: <b>PCT/FI99/00741</b>		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 13 September 1999 (13.09.99)		<b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>	
(30) Priority Data: 981959 11 September 1998 (11.09.98) FI			
(71) Applicant (for all designated States except US): ASM MICRO-CHEMISTRY LTD [FI/FI]; Kutojantie 2 B, FIN-02630 Espoo (FI).			
(72) Inventors; and (75) Inventors/Applicants (for US only): LESKELÄ, Markku [FI/FI]; Rauduntie 19 D, FIN-02130 Espoo (FI). RITALA, Mikko [FI/FI]; Antreantie 8 B 4, FIN-02140 Espoo (FI). HATANPÄÄ, Timo [FI/FI]; Aamuyönkuja 3 B, FIN-02210 Espoo (FI). HÄNNINEN, Timo [FI/FI]; Pitkäsillanranta 7 - 9 A 10, FIN-00530 Helsinki (FI). VEHKAMÄKI, Marko [FI/FI]; Rautalamminatie 3 B 409, FIN-00550 Helsinki (FI).			
(74) Agent: SEPPÖ LAINE OY; Itämerenkatu 3 B, FIN-00180 Helsinki (FI).			
(54) Title: METHOD FOR GROWING OXIDE THIN FILMS CONTAINING BARIUM AND STRONTIUM			
(57) Abstract <p>The present invention relates to a method for growing oxide thin films which contain barium and/or strontium. According to the method, such thin films are made by the ALE technique by using as precursors for barium and strontium their cyclopentadienyl compounds. A thin film made by means of the invention has a high permittivity and excellent conformality.</p>			

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

# Method for growing oxide thin films containing barium and strontium

The present invention relates to high permittivity oxide films and superconductive materials which contain barium and/or strontium. A particular object of the invention is the method according to the preamble of Claim 1 for producing such films and materials.

Dielectric thin films having high dielectric constants (permittivities) are required in many sub-areas of microelectronics and optoelectronics. In particular, the continual decrease in the size of microelectronics components has increased the need for the use of such dielectric films. For example, the capacitance of DRAM (Dynamic Random Access Memory) capacitors must remain nearly constant while their size decreases rapidly, and thus it is necessary to replace the previously used  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  with materials which have higher permittivities than these. In optoelectronics, dielectric films having high permittivities can be exploited in, for example, electroluminescence displays, in which the operating voltage of the displays can be reduced by means thereof. Some dielectric materials having high permittivities, e.g.  $\text{BaTiO}_3$ , are also ferroelectric materials at normal temperatures, a factor which further extends their potential uses, for example, to NVRAM (Nonvolatile Random Access Memory) and various microelectromechanical applications.

In addition to high permittivities, these dielectric thin films are required to have, among other things, low leakage current densities and high dielectric breakdown fields. The achievement of both of these properties presupposes a dense and flawless film structure. Of course, the properties of the films must be stable in the conditions of use. Furthermore, in particular in microelectronics applications, the conformality of the films, i.e. their capacity to cover surfaces of complicated shapes with a film of a uniform thickness is important, because in the manufacture of microelectronics components it is necessary to deposit films even in deep trenches and holes.

Oxide thin films containing barium and strontium are widely used and researched dielectric films having high permittivities. Important oxide thin films containing barium and strontium include, for example,  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  (x is 0-1). In addition to these there can be mentioned high-temperature superconductors, e.g.  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (x is 0-1),  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$  and  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$ , and dielectric materials lattice-

matched therewith,  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{Sr}_2\text{AlTaO}_6$  (D.L. Schulz and T.J. Marks, Advanced Materials 6 (1994) 719). In all of the above-mentioned formulae,  $n$  is 1-3 and  $\delta$  is 0-1. Other oxide films containing barium and strontium include various niobates  $(\text{Sr,Ba})\text{Nb}_2\text{O}_6$  and  $(\text{Pb,Ba})\text{Nb}_2\text{O}_6$  (L.M. Shepard, Ceramic Bulletin 71 (1992) 85). These films have been  
5 manufactured by many different methods, such as the sol-gel method, various physical vapor deposition methods (PVD) (e.g. vaporization, sputtering, laser ablation) and chemical vapor deposition methods (CVD).

Films manufactured by the sol-gel method, by various physical vapor deposition methods  
10 (PVD) (e.g. vaporization, sputtering, laser ablation) and by chemical vapor deposition methods (CVD) are of a high quality. Instead, the manufacture of a film of uniform quality and thickness when the surface structure of the piece is complicated will not succeed. Only by the CVD method is it possible to deposit conformal films in deep trenches and holes (S.M. Bilodeau, Solid State Technology, July (1997) 235). Even in the CVD method, high  
15 conformality is attained only when the rate of film growth is determined by the rate of the surface reaction and not by the diffusion of the precursors on the film surface. This is achieved when the surface reaction is slower than the diffusion of the precursors on the film surface. The surface reaction is slow at low temperatures, but in such a case the other properties of the film will, however, often remain poor, which is due to both the poor  
20 crystallinity of the film and to difficulties in the control of its composition (C.S. Kang et al., Japanese Journal of Applied Physics, Part 1 36 (1997) 6946; M. Kiyotoshi and K. Eguchi, Electrochemical Society Proceedings 97-25 (1997) 1063).

Atomic Layer Epitaxy (ALE), which is also known as Atomic Layer Chemical Vapor  
25 Deposition (ALCVD) or Atomic Layer Deposition (ALD), is a known method for the deposition of thin films (US patent publication 4.085.430). In this method, the thin film is deposited by means of alternate saturating surface reactions. These reactions are implemented by feeding gaseous or vaporized precursors into the reactor alternately and by purging the reactor with an inert gas between the precursor pulses (T. Suntola, Thin Solid  
30 Films 215 (1992) 84; Niinistö et al., Materials Science and Engineering B 41 (1996) 23). In addition, ALE can be used for depositing layers of uniform thickness even on large surfaces, and the control of the thickness and composition by means of the number of reaction cycles is precise and simple.

The ALE method has previously been used for making  $\text{TiO}_2$  films (Ritala et al., Thin Solid Films 225 (1993) 288, Chemistry of Materials 5 (1993) 1174 and 6 (1994) 556), but so far it has not been possible to manufacture the barium- and strontium-containing oxide thin films which are the object of the present invention by the ALE method in a self-controlling manner. Attempts at self-controlling deposition of superconductive films have also failed. The most important reason for not manufacturing the above-mentioned compounds is the lack of suitable precursors for Ba and Sr. Few of the compounds of the said elements are volatile, and so the precursors used in both CVD and ALE have as a rule been of one compound type, i.e.  $\beta$ -diketonates (W.A. Wojtcak et al., Advances in Organometallic Chemistry 40 (1996) 215, Tiitta and Niinistö, Chemical Vapor Deposition 3 (1997) 167). The problem with the  $\beta$ -diketonates of Ba and Sr is that they do not react with the oxygen sources,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_2$ , most typically used in the ALE method, at temperatures at which they would not decompose thermally. Iodides of the said metals have also been used in the CVD method (P. Mårtensson and A. Hårsta, Journal of Crystal Growth 156 (1995) 67), but in this case it is necessary to use temperatures which are too high for most applications.

EP application publication No. 344 352 describes a method for making laminated superconductors by an epitaxy method. The ALE method is also mentioned. The application publication also lists suitable organometallic compounds which can be used as precursors in these methods. Barium cyclopentadienyl is also among them. However, in the publication a film has not been deposited by specifically the ALE method and by using specifically barium cyclopentadienyl as the precursor. Furthermore, the EP publication does not provide preferred conditions for the film growth, since it does not state how or in what conditions cyclopentadienyl compounds should be used, how oxygen is introduced into the oxides or what advantages would follow specifically from the use of barium cyclopentadienyl as the precursor in any of the alternative epitaxy methods described in the publication.

It is an object of the present invention to eliminate the deficiencies described above and to provide a novel method for the manufacture of thin films and superconductive materials which contain barium and strontium.

The invention is based on the observation that the barium and strontium compounds

according to the invention are sufficiently stable in a gas phase, and consequently these compounds can be used as precursors in the ALE technique, and thus oxide thin films which contain barium and strontium can be deposited in a controlled manner. The cyclopentadienyl compounds of barium and strontium are such vaporizable compounds. In  
5 the deposition of film, the said barium and strontium compounds are used as precursors in a method according to the ALE principle together with a reactive oxygen precursor and a volatile titanium compound.

More specifically, the method according to the invention is characterized by what is stated  
10 in the characterizing part of Claim 1.

The invention will be discussed below with the help of the accompanying drawings.

Figure 1 depicts the composition of a multi-component film as a function of the cycle ratio  
15 of the various components.

Figure 2 depicts an X-ray diffraction analysis of the thin film.

Figure 3 depicts the permittivities of films deposited at 325 °C, as a function of the cycle  
20 ratio, as measured from the structure ITO/SrTiO<sub>3</sub>/Al, where ITO is indium-tin oxide.

In the technical solution according to the invention, oxide thin films are deposited in an ALE reactor at a temperature of 100-700 °C, preferably 150-400 °C. Either sheet-form (such as glass or silicon wafer) or pulverous materials can be used as the substrate.  
25 According to the ALE method, a cyclopentadienyl compound containing an earth-alkali metal is vaporized, whereafter the reactor is purged with an inert gas, the oxygen precursor is fed into the reactor, and the reactor is purged for a second time with an inert gas. All of these steps together constitute one deposition cycle. The deposition cycle is repeated until the film is of the desired thickness. A multi-component film is obtained by changing the  
30 precursor.

In connection with the present invention, cyclopentadienyl compounds of barium or strontium are used as precursors. By these compounds is meant any compound according to Formulae I-IV.

	$M(Cp)_2$	(I)
	$M(Cp)_2L_n$	(II)
	$M(Cp)X$	(III)
5	$M(Cp)XL_n$	(IV),

in which formulae

M is Ba or Sr;

10

Cp is a cyclopentadienyl group, the Cp groups present in Formulae I and II being mutually the same or different;

X is a ligand other than Cp, with the valency of -1;

15

$L_n$  is a neutral adduct ligand which binds to a metal by either one or several of its atoms, and n depicts the number of the ligands being bound.

20 In Formulae I-IV the cyclopentadienyl groups may also be in the same molecule. In this case the bridge between two Cp groups is made up of a substituted or unsubstituted  $C_1-C_6$  chain, which may contain a heteroatom which is Si, N, P, Se or S.

Ligand X is preferably  $\beta$ -diketonate or a corresponding sulfur or nitrogen compound, halide, amide, alkoxide, carboxylate or Schiff base.

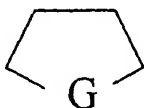
25

L is preferably

- (i) a hydrocarbon,
- (ii) an oxygen-containing hydrocarbon,
- (iii) a nitrogen-containing hydrocarbon,
- 30 (iv) a sulfur-containing hydrocarbon,
- (v) a phosphorus-containing hydrocarbon,
- (vi) an arsenic-containing hydrocarbon,
- (vii) a selenium-containing hydrocarbon, and/or
- (viii) a tellurium-containing hydrocarbon.

Most preferably L is

- (a) an amine or a polyamine,  
 (b) a bipyridine,  
 5 (c) a ligand depicted by the formula



(V)

10

in which formula G is -O-, -S-, or -NR<sup>1</sup>-, where R<sup>1</sup> is hydrogen or a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, cyano or silyl group. The cyclic or aromatic ring of R<sup>1</sup> may contain a heteroatom. The ligand depicted by Formula V may also have either hydrogen or

15

(d) ether or thioether.

The cyclopentadienyl group (Cp) in Formulae I-IV is of the form

20



where m is an integer of 0-5,

Cp' is a fused or individual cyclopentadienyl, and

25

R is a hydrocarbon radical containing 1-20 carbon atoms, preferably a C<sub>1</sub>-C<sub>6</sub> hydrocarbon. The R's may be mutually the same or different. R may be a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, amino, cyano or silyl group. The cyclic or aromatic ring of the substituent may contain a heteroatom. Methyl, ethyl, propyl and isopropyl groups can be mentioned as examples of the substituents.

30

Preferably there is used an organometallic complex according to Formula II, where Cp is cyclopentadienyl, indenyl or fluorenyl. As the neutral adduct ligand L (Formulae II and IV) there are used, for example, ethers, amines or solvent molecules (e.g. tetrahydrofuran) which bind to the metal by one atom. Polyethers and polyamines can be mentioned as examples of suitable ligands which bind to the metal by several of their atoms.



According to the invention, the precursor used for the oxide thin film is especially preferably a THF adduct of bis(pentamethylcyclopentadienyl) or bis(triisopropylcyclopentadienyl) of barium or strontium.

5

According to the first preferred embodiment of the invention, the cyclopentadienyl compounds of barium and strontium are used together with a volatile titanium compound (e.g. a halide, alkoxide, cyclopentadienyl, alkylamide) and a reactive oxygen precursor (e.g.  $H_2O$ ,  $H_2O_2$ ), in which case  $BaTiO_3$ ,  $SrTiO_3$  and  $Ba_{1-x}Sr_xTiO_3$  films can be grown by  
10 the ALE method at low deposition temperatures ( $325^\circ C$ ). The said precursors can also be exploited in ALE deposition of other oxide thin-films containing barium and/or strontium.

Below there are listed titanium compounds which have vapor pressures sufficient at a temperature lower than the temperature of the deposition substrate, and which are thus  
15 suitable for use in the method according to the present invention. Thus, preferably one or more of the following compounds are used as the volatile titanium compound:

- titanium halides, for example  $TiCl_4$ ,  $TiCl_3$ ,  $TiBr_3$ ,  $TiI_4$ ,  $TiI_3$ ,
- titanium alkoxides, for example  $Ti(OC_2H_5)_4$ ,  $Ti(O^iPr)_4$ ,  $Ti(O^tBu)_4$  and titanium(IV)-ethylhexoxide,
- 20 - titanium nitrate ( $Ti(NO_3)_4$ ),
- alkylamino complexes of titanium, for example tetrakis(diethylamino)titanium, tetrakis(dimethylamino)titanium, tetrakis(ethylmethylamino)titanium, tetrakis(isopropylmethylamino)titanium, bis(cyclopentadienyl)bis(dimethylamino)titanium, tris(dimethylamino)(N,N,N'-trimethylethyldiamino)titanium, and tert-butyltris(dimethylamino)titanium; further examples of applicable compounds  
25 are described in US patent No. 5,659,057,
- cyclopentadienyl complexes of titanium, for example  $Ti(\eta^5-C_5H_5)_2$ ,  $Ti(\eta^5-C_5H_5)(\eta^7-C_7H_7)$ ,  $(\eta^5-C_5H_5)TiR_2$ , where  $R = \text{alkyl (e.g. } CH_3\text{), benzyl (} C_6H_5\text{) or carbonyl, bis(t-butylcyclopentadienyl)titanium dichloride, bis(pentamethylcyclopentadienyl) titanium dichloride, and } (C_5H_5)_2Ti(CO)_2$ ,
- 30 - silylamido complexes of titanium, such as  $Ti\{N_4[Si(CH_3)_3]_4[Si(CH_3)_2]_2\}$ ; further examples of applicable compounds are described in US patent No. 5,603,988,
- titaniumdialkyldithiocarbamates, and
- titanium- $\beta$ -diketonates, for example di(i-propoxide)bis(2,2,6,6-tetramethyl-3,5-

heptanedionato)titanium, and tris(2,2,6,6,-tetramethyl-3,5-heptanedionato)-titanium(III).

Especially preferably, titanium tetraisopropoxide ( $\text{Ti}(\text{O}^i\text{C}_3\text{H}_7)_4$ ) is used.

5

The oxygen precursor may be any oxygen compound usable in the ALE technique. Preferable oxygen precursors include water, oxygen and hydrogen peroxide, and aqueous solutions of hydrogen peroxide. Ozone ( $\text{O}_3$ ) is an especially preferable oxygen precursor. It is known on the basis of the literature that, if ozone is used as the precursor for oxygen, a denser layer of material is obtained from the forming oxides, and thereby the permittivity of the oxide thin film can be improved.

10

One or more of the following compounds may also be used as the precursor for oxygen:

- oxides of nitrogen, such as  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{NO}_2$ ,
- 15 - halide-oxygen compounds, for example chlorine dioxide ( $\text{ClO}_2$ ) and perchloric acid ( $\text{HClO}_4$ ), the compatibility of these with earth-alkali metals being, however, limited,
- peracids ( $-\text{O}-\text{O}-\text{H}$ ), for example perbenzoic acid ( $\text{C}_6\text{H}_5\text{COOOH}$ ) and peracetic acid ( $\text{CH}_3\text{COOOH}$ ),
- 20 - alcohols, such as methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), and
- various radicals, for example oxygen radical ( $\text{O}^\cdot$ ) and hydroxyl radical ( $\cdot\text{OH}$ ).

20

According to a second preferred embodiment, the ratio of the deposition cycles (e.g.  $\text{Ti}-\text{O}$ ,  $\text{Sr}-\text{O}$  and  $\text{Ba}-\text{O}$ ) producing the different binary oxides of multicomponent oxide films (e.g.  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ) is controlled. If, for example,  $\text{Sr}/\text{Ti}$  is 0.8-1.2, preferably approx. 1, a crystalline film is obtained (cf. Example 1). Thus the composition can be controlled simply and with precision. In order that the composition of the film should be uniform, the deposition cycles are carried out so that the different materials become mixed as completely as possible, i.e. there will be 1-10, preferably 1-2 similar cycles in succession.

30

According to a third preferred embodiment, the oxide film is grown at a lower temperature (250-300 °C), whereby an amorphous thin film is obtained. The structure of the film

becomes crystalline during postannealing. The postannealing is carried out at a temperature higher than the growth temperature, and its duration may vary. According to a preferred embodiment of the invention, the duration of the postannealing is 60 min, and it is carried out in an air stream at 500 °C.

5

Considerable advantages are gained with the help of the invention. Since according to the ALE method the film grows through saturating surface reactions, the growth is self-controlling, which in turn ensures excellent conformality. As is evident from the above, cyclopentadienyl compounds of strontium and barium can be used as vaporizing components within a wide temperature range, in which case the structure of the thin film made and its crystallinity can be effectively controlled by the selection of the reaction temperature and the metal mixing ratio and by a potential post-treatment. The present precursors are especially advantageous for use in the ALE technique also for the reason that they will not leave significant carbon or hydrogen residues in the final product. On the other hand, the dielectric constants of oxide thin films containing barium and strontium are very high, and thus the oxides of specifically barium and strontium are especially suitable as materials for dielectric thin films. Owing to their high dielectric constants they are especially suitable for memory circuits and for gate oxides. By the use of cyclopentadienyl compounds of barium together with a volatile titanium compound, a low-temperature growth process is achieved, which is important in most applications of dielectric films.

In the context of the present invention, by dielectric oxide thin film is meant a thin film having a high permittivity. The permittivity varies according to the thickness of the film so that the permittivity of a thinner film is lower. It can be noted as an example that for a film approx. 50 nm thick a high permittivity is approx. 50 or more, preferably approx. 100 or more.

Thin films according to the invention are preferably used as dielectric films of various electronics components. Films according to the invention are deposited, for example, on platinum (Pt), RuO<sub>2</sub>, IrO<sub>2</sub>, SrRuO<sub>3</sub>, LaSrCoO<sub>3</sub>, IrO<sub>2</sub>/Ir, RuO<sub>2</sub>/Pt, silica (SiO<sub>2</sub>), silicon nitride and silicon surfaces.

By means of the present invention it is possible to make, in addition to the above-mentioned thin films, also high-temperature superconductors mentioned in the preamble,

for example  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x$  is 0-1),  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$  and  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$ , and dielectric materials lattice-matched therewith, such as  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , and  $\text{Sr}_2\text{AlTaO}_6$  (D. L. Schulz and T. J. Marks, *Advanced Materials* 6 (1994) 719).

- 5 Three examples are presented below in order to illustrate the invention.

#### Example 1

- 10  $\text{SrTiO}_3$  films were grown in a flow-type F-120 ALE reactor (Mikrokemia Oy) at a temperature of 325 °C. The strontium precursor used was the THF adduct of bis(triisopropylcyclopentadienyl) strontium,  $\text{Sr}(\text{C}_5(\text{C}_3\text{H}_7)_2)_2\text{THF}_p$ , in which  $p = 0-2$  and THF is tetrahydrofuran, and which was vaporized in the reactor by heating it to a temperature of 100 °C. The titanium precursor used was titanium tetraisopropoxide
- 15  $(\text{Ti}(\text{O}(\text{C}_3\text{H}_7)_2)_4)$ , which was vaporized in the reactor at a temperature of 40 °C. The oxygen source used was water, which was fed into the reactor from outside it. The growth of  $\text{TiO}_2$  from the said precursors has been described previously (Ritala et al., *Chemistry of Materials* 5 (1993) 1174).
- 20 The growth of  $\text{SrTiO}_3$  was implemented by using alternate Ti-O and Sr-O deposition cycles. The Ti-O cycle was made up of four steps: (i) an 0.6 s pulse of  $\text{Ti}(\text{O}(\text{C}_3\text{H}_7)_2)_4$ , an 0.5 s purge with inert nitrogen gas, (iii) an 0.6 pulse of  $\text{H}_2\text{O}$ , and (iv) an 0.5 s purge with nitrogen gas. Respectively, the composition of the Sr-O cycle was: (i) an 0.6 s pulse of  $\text{Sr}(\text{C}_5(\text{C}_3\text{H}_7)_2)_2\text{THF}_p$ , (ii) an 0.5 s purge with nitrogen gas, (iii) an 0.5 s pulse of  $\text{H}_2\text{O}$ , and (iv)
- 25 an 0.5 s purge with nitrogen gas. The composition of the film was controlled by the ratio of the Ti-O and Sr-O cycles. The alternation of the Ti-O and Sr-O cycles was implemented so that there were at maximum two similar cycles in succession. For example, the cycle ratio Ti-O/Sr-O = 1:1 was achieved by repeating the cycling formula  $q[(\text{Ti-O})(\text{Sr-O})]$  and the ratio Ti-O/Sr-O = 3:4 by means of the formula  $q[(\text{Ti-O})(\text{Sr-O})(\text{Ti-O})(\text{Sr-O})(\text{Ti-O})(\text{Sr-O})]$ , in which formulae  $q$  indicates how many times the said cycling was repeated.
- 30 Thus  $q$  determines the thickness of the film.

When the films were grown at a temperature of 325 °C, their composition varied according to the cycle ratio (Figure 1). The linearity of the curve shown in the figure is an indication

that the composition can well be controlled by means of the cycle ratio. Films having Sr/Ti ratios close to 1 were, according to an X-ray diffraction analysis, crystalline  $\text{SrTiO}_3$  (Figure 2). TOF-ERDA (Time-of-Flight Elastic Recoil and Detection Analysis) showed that the films contained carbon and hydrogen residues lower than 0.2 at.%, the other possible impurity residues being so low that they cannot be detected by the method concerned.

Figure 3 shows the effect of the post-treatment on the permittivity of the film. The permittivities of films without post-treatment are at maximum 118, but annealing in air at a temperature of 500 °C for 60 min increases permittivity significantly, the highest values being 180. The postannealing also increased the intensity of X-ray reflections, showing an improved film crystallinity.

#### Example 2

The process according to Example 1 was repeated using a growth temperature of 250 °C. The films thus grown were amorphous, but they crystallized when they were heated in air at 500 °C for 60 min.

#### Example 3

$\text{BaTiO}_3$  films were grown in the manner described in Example 1, but by using instead of  $\text{Sr}(\text{C}_5(\text{C}_3\text{H}_7)_2)_2\text{THF}_x$  a THF adduct of bis(pentamethylcyclopentadienyl)barium,  $\text{Ba}(\text{C}_5(\text{CH}_3)_4)\text{THF}_x$ , where  $x = 0-2$ . The deposition temperature was 250 °C. When a deposition cycle ratio of  $(\text{Ti-O})/(\text{Ba-O}) = 6:5$  was used, an amorphous film was obtained. When this film was heated in air at 500 °C for 60 min, it crystallized as  $\text{BaTiO}_3$ , for which a measurement showed a permittivity of 165.

## Claims:

1. A method for growing oxide thin films, characterized in that the films are produced by the ALE process by using as the precursor cyclopentadienyl compounds of strontium and/or barium, together with one or more volatile titanium compounds and a reactive oxygen precursor.
2. The method according to Claim 1, characterized in that the oxide thin film to be grown is dielectric.
3. The method according to Claim 1 or 2, characterized in that there are 1-10, preferably 1-2, similar growth cycles in succession, one growth cycle being made up of the feeding of a Ba compound, Sr compound or volatile titanium compound; an inert purge; the feeding of a precursor for oxygen; and a second inert purge.
4. The method according to any of Claims 1 - 3, characterized in that the cycle ratio of the alkaline earth metal compound and the titanium compound is 0.8-1.2.
5. The method according to any of Claims 1 - 4, characterized in that the volatile titanium compound is a titanium halide, titanium alkoxide, titanium nitrate ( $\text{Ti}(\text{NO}_3)_4$ ), an alkylamino complex of titanium, a cyclopentadienyl complex of titanium, a silylamido complex of titanium, titanium dialkyldithiocarbamate, or titanium- $\beta$ -diketonate.
6. The method according to any of the preceding claims, characterized in that the film growth substrate is a platinum (Pt),  $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{SrRuO}_3$ ,  $\text{LaSrCoO}_3$ ,  $\text{IrO}_2/\text{Ir}$ ,  $\text{RuO}_2/\text{Pt}$ , silica ( $\text{SiO}_2$ ), silicon nitride or silicon surface.
7. The method according to any of the preceding claims, characterized in that the reactive oxygen precursor used is oxygen ( $\text{O}_2$ ), water vapor, hydrogen peroxide or an aqueous solution of hydrogen peroxide, and/or ozone.
8. The method according to any of the preceding claims, characterized in that the formula of the precursor is  $\text{M}(\text{Cp})_2$  or  $\text{M}(\text{Cp})_2\text{L}_n$ , where
  - M is Sr or Ba,

- Cp is a fused or single cyclopentadienyl group of the form  $\text{Cp}'\text{R}_m\text{H}_{5-m}$ , where
  - m is an integer 0-5 and
  - R is a hydrocarbon group, the hydrocarbon groups being mutually either the same or different,
- 5 - the Cp groups are either the same or different,
- $\text{L}_n$  is a neutral adduct ligand which binds to the metal by one or several of its atoms.

9. The method according to any of Claims 1 - 7, characterized in that

- the precursor for Sr and/or Ba is of the form  $\text{M}(\text{Cp})\text{X}$  or  $\text{M}(\text{Cp})\text{XL}_n$ , where
- M is Sr or Ba,
- Cp is a fused or single cyclopentadienyl group  $\text{Cp}'\text{R}_m\text{H}_{5-m}$ , where
  - m is an integer 0-5 and
  - 15 - R is a hydrocarbon group, the R's being mutually either the same or different,
- X is a ligand, other than Cp, having a valence of -1 and
- L is a neutral adduct ligand which binds to the metal by one or several of its atoms.

20

10. The method according to Claim 8 or 9, characterized in that the cyclopentadienyl group is cyclopentadienyl, pentamethylcyclopentadienyl, triisopropylcyclopentadienyl, indenyl, or fluorenyl.

25 11. The method according to Claim 8 or 9, characterized in that the Cp groups are contained in the same molecule.

12. The method according to Claim 11, characterized in that the bridge between two Cp groups is made up of a substituted or unsubstituted  $\text{C}_1 - \text{C}_6$  carbon chain.

30

13. The method according to Claim 12, characterized in that the carbon chain forming the bridge contains a heteroatom, which is silicon, nitrogen, phosphorus, selenium, or sulfur.

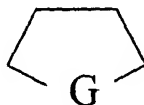
14. The method according to Claim 8 or 9, characterized in that R is a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, amino, cyano or silyl group.

15. The method according to Claim 8 or 9, characterized in that the neutral adduct ligand L is

- (i) a hydrocarbon,
- (ii) an oxygen-containing hydrocarbon,
- (iii) a nitrogen-containing hydrocarbon,
- (iv) a sulfur-containing hydrocarbon,
- (v) a phosphorus-containing hydrocarbon,
- (vi) an arsenic-containing hydrocarbon,
- (vii) a selenium-containing hydrocarbon, and/or
- (viii) a tellurium-containing hydrocarbon.

16. The method according to Claim 8 or 9, characterized in that L is

- (a) an amine or polyamine,
- (b) a bipyridine,
- (c) a ligand depicted by the formula



(V)

in which formula G is -O-, -S-, or -NR<sup>1</sup>-, where R<sup>1</sup> is hydrogen or a substituted or unsubstituted, cyclic, linear or branched, alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, cyano or silyl group, and in each carbon atom of the ring according to the formula there is an R<sup>1</sup>-like substituent, which are either mutually the same or different,

- (d) ether, or
- (e) thioether.

17. The method according to Claim 8 or 9, wherein L is an ether, polyether, amine, polyamine, bipyridine or tetrahydrofuran.



18. The method according to Claim 9, characterized in that X is a  $\beta$ -ketonate or a corresponding sulfur or nitrogen compound, alkyl, halide, amide, alkoxide, carboxylate or Schiff base.

5

19. The method according to any of the preceding claims, characterized in that the growth of the film takes place at 250-300 °C, and the postannealing carried out after the growth takes place at a temperature higher than the deposition temperature, preferably at 500 °C.

1/3

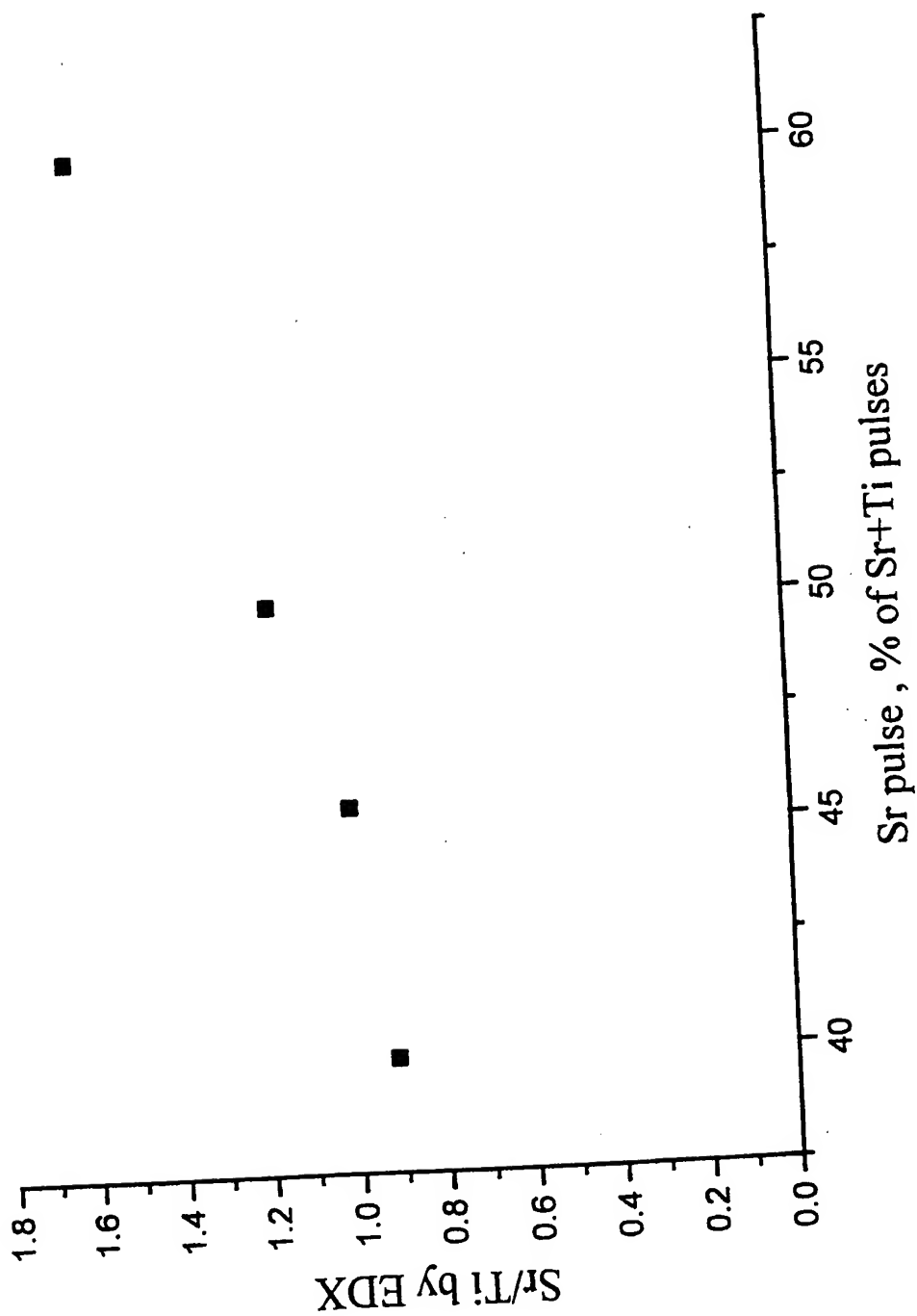


Fig. 1

2/3

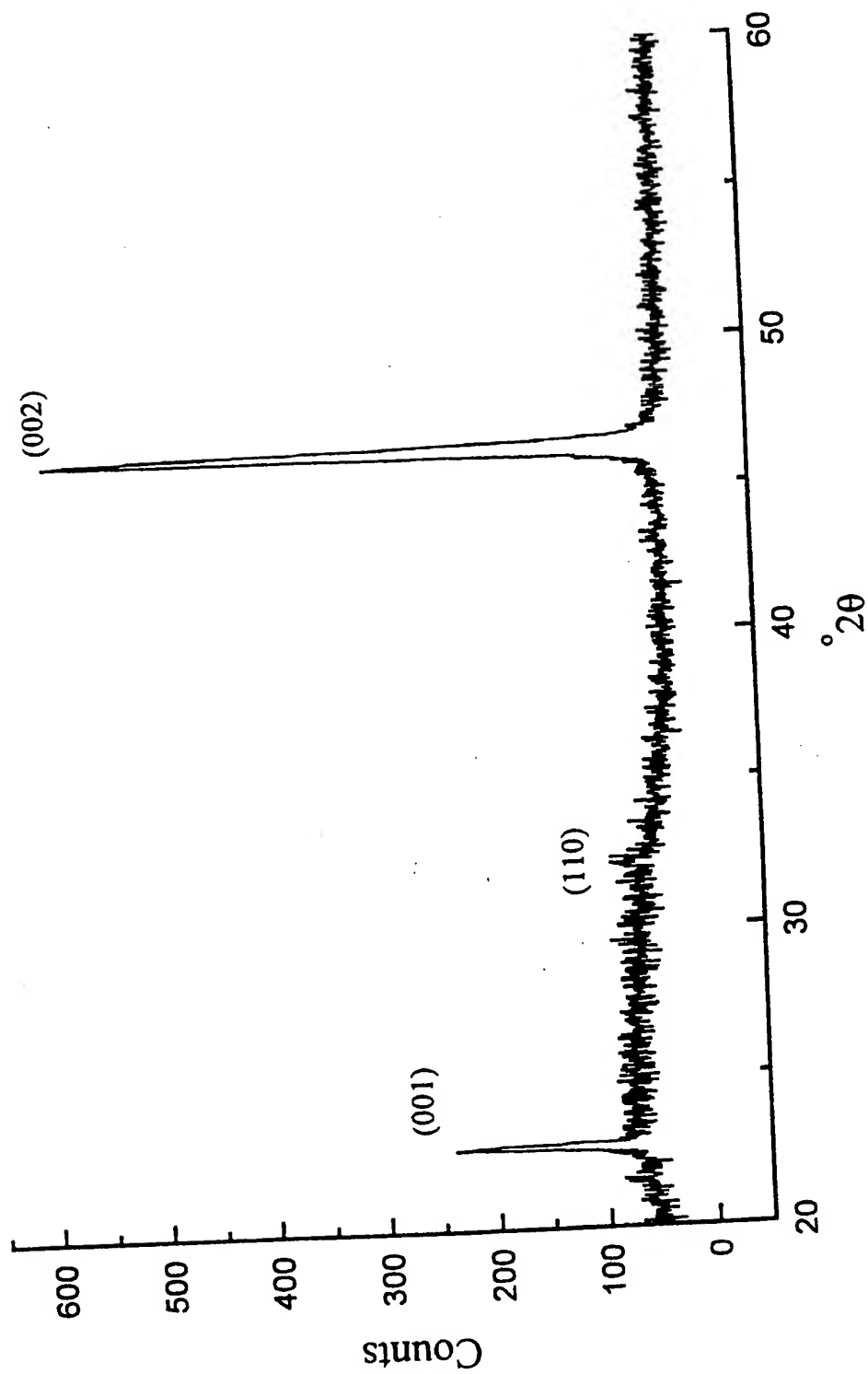


Fig. 2

3/3

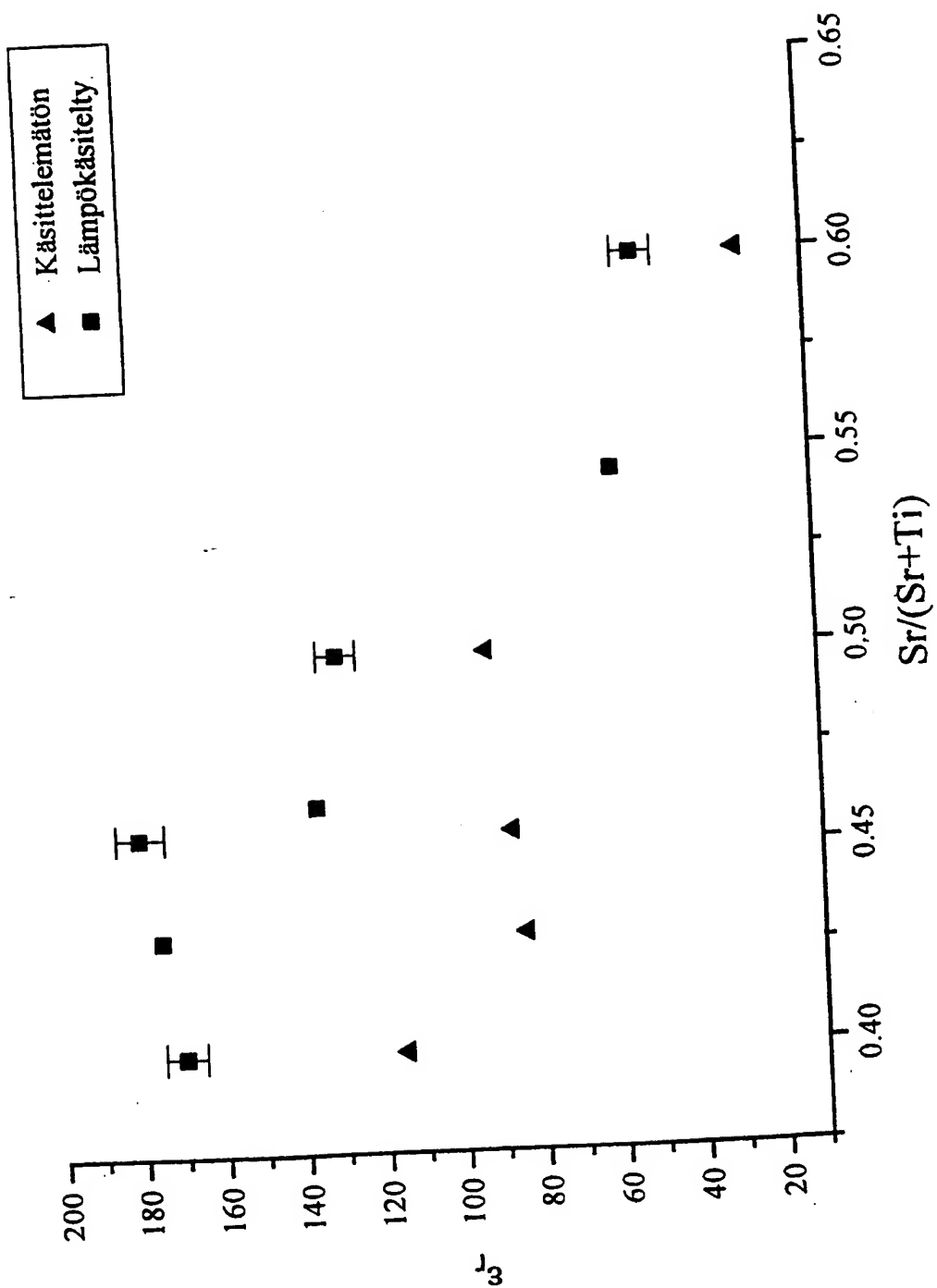


Fig. 3

1  
INTERNATIONAL SEARCH REPORT

International application No.  
PCT/FI 99/00741

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC7: C23C 16/00, C23C 16/44, C30B 25/02, C30B 29/22, H01L 39/24, H01L 39/12  
According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C23C, C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0344352 A1 (INTERNATIONAL BUSINESS MACHINES CORPORATION), 6 December 1989 (06.12.89), page 3, line 46 - page 4, line 15; page 5, line 8 - line 20; page 6, line 2 - line 11, abstract --	1-19
X	US 4927670 A (AHMET ERBIL), 22 May 1990 (22.05.90), column 2, line 58 - line 59; column 3, line 65 - column 4, line 11; column 5, line 18 - line 22, column 8, line 35 - line 49; column 11, line 31 - line 33, abstract --	1-19
X	FR 2626110 A1 (THOMSON CSF), 21 July 1989 (21.07.89), page 5, line 11 - line 23; page 6, line 1 - line 30, figure 2 --	1-19

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document but published on or after the international filing date	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search	Date of mailing of the international search report
2 December 1999	14 -12- 1999
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Ulrika Nilsson/ELY Telephone No. +46 8 782 25 00

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 99/00741

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4058430 A (TUOMO SUNTOLA ET AL), 15 November 1977 (15.11.77), abstract  --	1-19
A	Materials Science and Engineering, Volume B41, 1996, Lauri Niinistö et al, "Synthesis of oxide thin films and overlayers by atomica layer epitaxy for advanced applications", page 23 - page 29, page 27, column 2, line 44 - page 28, column 1, line 17  -- -----	19

INTERNATIONAL SEARCH REPORT  
Information on patent family members

02/11/99

International application No.

PCT/FI 99/00741

Patent document cited in search report.	Publication date	Patent family member(s)	Publication date
EP 0344352 A1	06/12/89	SE 0344352 T3 AT 112418 T CA 1330193 A DE 3851701 D,T JP 7061920 B US 5439876 A	15/10/94 14/06/94 30/03/95 05/07/95 08/08/95
US 4927670 A	22/05/90	NONE	
FR 2626110 A1	21/07/89	NONE	
US 4058430 A	15/11/77	AT 381122 B AT 868675 A AU 505960 B AU 8666275 A BE 835906 A BR 7507724 A CA 1066174 A CH 618469 A CS 249502 B DD 122479 A DE 2553048 A,B,C DK 152060 B,C DK 539875 A FI 52359 B,C FI 347374 A FR 2292517 A,B GB 1495987 A HK 64880 A IN 143912 A JP 1147355 C JP 51077589 A JP 57035158 B NL 173824 B,C NL 7513284 A SE 393967 B,C SE 401986 B,C SE 7513336 A ZA 7507128 A	25/08/86 15/01/86 06/12/79 26/05/77 16/03/76 10/08/76 13/11/79 31/07/80 12/03/87 12/10/76 10/06/76 25/01/88 30/05/76 02/05/77 30/05/76 25/06/76 21/12/77 21/11/80 05/02/78 26/05/83 05/07/76 27/07/82 17/10/83 01/06/76 31/05/77 12/06/78 31/05/76 27/10/76

 Powered by **DIALOG**ORDER  
ORIGINAL**Basic Patent (Number,Kind,Date):** FI 9801959 A0 19980911**Patent Family:**

Patent Number	Kind	Date	Application Number	Kind	Date
AU 9957483	A1	20000403	AU 9957483	A	19990913
FI 9801959	A	20000312	FI 981959	A	19980911
FI 9801959	A0	19980911	FI 981959	A	19980911 (Basic)
WO 200015865	A1	20000323	WO 99FI741	A	19990913

**Priority Data:**

Patent Number	Kind	Date
FI 981959	A	19980911
WO 99FI741	W	19990913

**PATENT FAMILY:****Australia (AU)**

**Patent (Number,Kind,Date):** AU 9957483 A1 20000403  
**METHOD FOR GROWING OXIDE THIN FILMS CONTAINING BARIUM AND STRONTIUM (English)**  
**Patent Assignee:** ASM MICROCHEMISTRY LTD  
**Author (Inventor):** LESKELA MARKKU; RITALA MIKKO; HATANPAA TIMO; HANNINEN TIMO; VEHKAMAKI MARKO  
**Priority (Number,Kind,Date):** FI 981959 A 19980911; WO 99FI741 W 19990913  
**Applic (Number,Kind,Date):** AU 9957483 A 19990913  
**IPC:** \* C23C-016/00; C23C-016/44; C30B-025/02; C30B-029/22; H01L-039/24; H01L-039/12  
**CA Abstract No:** \* 132(17)230739W  
**Derwent WPI Acc No:** \* C 2000-292703  
**Language of Document:** English

**Finland (FI)**

**Patent (Number,Kind,Date):** FI 9801959 A 20000312  
**MENETELMAE BARIUMIA JA STRONTIUMIA SISAELETAEVIN OKSIDIOHUTKALVOJEN KASVATTAMISEKSI FOERFARANDE FOER FRAMSTAELLNING AV OXIDTUNNFILMER SOM INNEHAALLER BARIUM OCH STRONTIUM (Swedish)**  
**Patent Assignee:** MIKROKEMIA OY (FI)  
**Author (Inventor):** LESKELAE MARKKU ANTERO (FI); RITALA MIKKO KALERVO (FI); HATANPAEAE TIMO TAPIO (FI); HAENNINEN TIMO PEKKA (FI); VEHKAMAEKIMARKO JUHANI (FI)



Priority (Number,Kind,Date): FI 981959 A 19980911  
 Applic (Number,Kind,Date): FI 981959 A 19980911  
 IPC: \* H01L-039/24; H01L-039/14; C23C-016/00; C23C-016/44; C30B-025/02; C30B-029/22  
 CA Abstract No: \* 132(17)230739W  
 Derwent WPI Acc No: \* C 2000-292703  
 Language of Document: Finnish; Swedish  
 Patent (Number,Kind,Date): FI 9801959 A0 19980911  
 MENETELMAE BARIUMIA JA STRONTIUMIA SISAELTAEVIEN  
 OKSIDIOHUTKALVOJEN KASVATTAMISEKSI FOERFARANDE FOER FRAMSTAELLNING  
 AV OXIDTUNNFILMER SOM INNEHAALLER BARIUM OCH STRONTIUM (Swedish)  
 Patent Assignee: LESKELAE MARKKU ANTERO (FI); RITALA MIKKO KALERVO (FI);  
 HATANPAEAE TIMO TAPIO (FI); HAENNINEN TIMO PEKKA (FI); VEHKAMAEMI  
 MARKO JUHANI (FI)  
 Author (Inventor): LESKELAE MARKKU ANTERO (FI); RITALA MIKKO KALERVO (FI);  
 HATANPAEAE TIMO TAPIO (FI); HAENNINEN TIMO PEKKA (FI); VEHKAMAEMI  
 MARKO JUHANI (FI)  
 Priority (Number,Kind,Date): FI 981959 A 19980911  
 Applic (Number,Kind,Date): FI 981959 A 19980911  
 IPC: \* H01L  
 CA Abstract No: \* 132(17)230739W  
 Derwent WPI Acc No: \* C 2000-292703  
 Language of Document: Finnish; Swedish

#### Finland (FI) - Legal Status

Number	Type	Date	Code	Text	
FI 981959	A	19980911	FI AE	New application filed	(Uusi hakemus)
				FI 981959 A 19980911	
FI 981959	A	19990615	FI GB	Transfer of assignment of application	(Hakemus siirretty toiselle hakijalle)
				Mikrokemia Oy	

#### World Intellectual Property Organization, PCT (WO)

Patent (Number,Kind,Date): WO 200015865 A1 20000323  
 METHOD FOR GROWING OXIDE THIN FILMS CONTAINING BARIUM AND  
 STRONTIUM (English)  
 Patent Assignee: ASM MICROCHEMISTRY LTD (FI); LESKELAE MARKKU (FI); RITALA  
 MIKKO (FI); HATANPAEAE TIMO (FI); HAENNINEN TIMO (FI); VEHKAMAEMI  
 MARKO (FI)  
 Author (Inventor): LESKELAE MARKKU (FI); RITALAMIKKO (FI); HATANPAEAE  
 TIMO (FI); HAENNINEN TIMO (FI); VEHKAMAEMI MARKO (FI)  
 Priority (Number,Kind,Date): FI 981959 A 19980911  
 Applic (Number,Kind,Date): WO 99FI741 A 19990913  
 Designated States: (National) AE; AL; AM; AT; AU; AZ; BA; BB; BG; BR; BY; CA; CH; CN;  
 CR; CU; CZ; DE; DK; DM; EE; ES; FI; GB; GD; GE; GH; GM; HR; HU; ID; IL; IN; IS; JP; KE;  
 KG; KP; KR; KZ; LC; LK; LR; LS; LT; LU; LV; MD; MG; MK; MN; MW; MX; NO; NZ; PL; PT;  
 RO; RU; SD; SE; SG; SI; SK; SL; TJ; TM; TR; TT; UA; UG; US; UZ; VN; YU; ZA;  
 ZW (Regional) GH; GM; KE; LS; MW; SD; SL; SZ; UG; ZW; AM; AZ; BY; KG; KZ; MD; RU;  
 TJ; TM; AT; BE; CH; CY; DE; DK; ES; FI; FR; GB; GR; IE; IT; LU; MC; NL; PT; SE; BF; BJ; CF;  
 CG; CI; CM; GA; GN; GW; ML; MR; NE; SN; TD; TG  
 Filing Details: WO 100000 With international search report  
 IPC: \* C23C-016/00; C23C-016/44; C30B-025/02; C30B-029/22; H01L-039/24; H01L-039/12  
 CA Abstract No: \* 132(17)230739W; 132(17)230739W  
 Derwent WPI Acc No: \* C 2000-292703; C 2000-292703  
 Language of Document: English

## World Intellectual Property Organization, PCT (WO) - Legal Status

Number	Type	Date	Code	Text
WO 200015865	P	19980911	WO AA	PRIORITY (PATENT)
				FI 981959 A 19980911
WO 200015865	P	19990913	WO AE	APPLICATION DATA (APPL. DATA)
				WO 99FI741 A 19990913
WO 200015865	P	20000323	WO AK	DESIGNATED STATES CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT (DESIGNATED STATES CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
				AE AL AM AT AU AZ BA BB BG BR BY CACH CN CR CU CZ DE DK DM EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MD MG MK MN MW MX NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT UA UG US UZ VN YU ZA ZW
WO 200015865	P	20000323	WO AL	DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPLICATION WITH SEARCH REPORT (DESIGNATED COUNTRIES FOR REGIONAL PATENTS CITED IN A PUBLISHED APPL. WITH SEARCH REPORT)
				GH GM KE LS MW SD SL SZ UG ZW AM AZ BY KG KZ MD RU TJ TM AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG
WO 200015865	P	20000323	WO A1	PUBLICATION OF THE INTERNATIONAL APPLICATION WITH THE INTERNATIONAL SEARCH REPORT (PUB. OF THE INTERNATIONAL APPL. WITH THE INTERNATIONAL SEARCH REPORT)
WO 200015865	P	20000517	WO 121	EP: ALL PREREQUISITES FOR ENTERING THE EUROP. PHASE FULFILED
WO 200015865	P	20000608	WO DFPE	REQUEST FOR PRELIMINARY EXAMINATION FILED PRIOR TO EXPIRATION OF 19TH MONTH FROM PRIORITY DATE

INPADOC/Family and Legal Status

© 2001 European Patent Office. All rights reserved.

Dialog® File Number 345 Accession Number 14787645